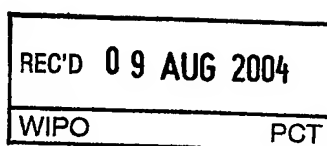




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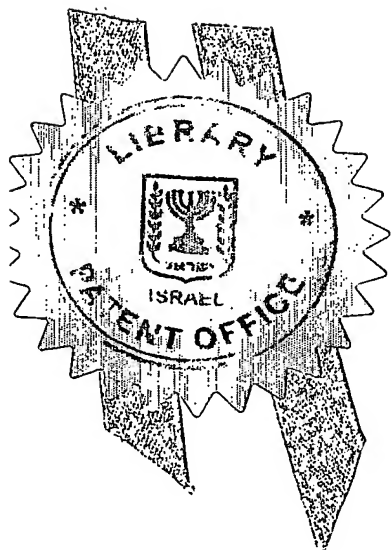
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of an invention the title of which

בעל ההמצאה מכח
ששמה הוא

תהליך להכנת וולקאניזאטים תרמופלסטיים

(בעברית)
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PROCESS FOR MAKING THERMOPLASTIC VULCANIZATES

(באנגלית)
(English)

hereby apply for a patent to be granted to me in respect thereof. מבקש בזאת כי ינתן לי עליה פטנט

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חתימת המבקש Signature of Applicant		היום 6 בחודש יולי שנה 2003 of the year of This				
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By: 
Attorneys for Applicant

טופס זה כשהוא מוטבע בחותם לישכת הפטנטים ומושלים במספר ובתאריך ההגשה, הינו אישור להגשת הבקשה שפרטיה רשומים לעיל.



16020/03



תהליך להכנת וולקאניזאטים תרמופלסטיים

PROCESS FOR MAKING THERMOPLASTIC VULCANIZATES

Process for Making Thermoplastic Vulcanizates

Field of the Invention

This invention relates to a process for making thermoplastic vulcanizates (hereinafter, briefly, TPVs) and to the products obtained from said process. The term "vulcanization" was traditionally used to designate the cross-linking of natural rubber by sulfur bridges, but has become more generally used, and so is used herein, to designate a process that leads to the cross-linking of elastomers.

Background of the Invention

Thermoplastic vulcanizates (TPVs) are a class of polymer materials comprising a continuous phase (matrix) usually of partially crystalline thermoplastic polymer (such as polypropylene and propylene copolymers) and a cross-linked ("vulcanized") disperse phase, usually elastomeric. TPVs were developed to close the gap between thermoplastic elastomers and thermoset rubbers. Having rubber-like properties (soft touch, resilience) and being processable by methods used for thermoplastic, these materials have better cost-performance ratios than traditional thermoset rubbers in certain applications.

A process specially designed to produce TPVs is dynamic vulcanization (hereinafter, briefly, DV). DV is based on cross-linking of disperse phase material during intensive shear mixing, thus preventing it to form a continuous phase. This process also generally includes phase inversion. Being usually a majority in the initial blend, the vulcanizable material forms a continuous phase, while the second component forms a disperse phase. However, the vulcanizing process leads to an increase in the viscosity of the vulcanized polymer, while the viscosity of non-cross-linked components remains unchanged or even slightly decreases. When the

viscosity of the cross-linked phase becomes significantly higher than that of the said second component, the vulcanized phase begins to break into droplets, that decrease in size as the viscosity increases. At this stage, phase inversion occurs, i.e., the non-cross-linked component changes from a disperse phase to a continuous matrix, while the vulcanized component changing from a matrix to a disperse phase. The phase inversion allows to obtain TPVs with well-defined phase structure, even at very high cross-linked phase contents (70% and higher).

DV processes may be implemented as batch (using batch mixers such as Banbury) or as continuous (using compounding equipment, e.g., twin-screw extruders). The continuous process has obvious advantages (higher output, better product uniformity, lower labor costs), but the residence time in the processing equipment is significantly shorter, requiring highly efficient cross-linking system to complete the reaction inside said equipment and to prevent post-curing during the following shaping and use of the resulting products.

It should be noted that it is not required that a matrix polymer (by which expression is meant the non-cross linked component that constitutes the matrix after phase inversion has occurred) of a TPVs be absolutely insensitive to the condition in which the elastomeric phase is vulcanized to form TPVs. Some reaction between the matrix and the vulcanization agents may occur, and may even be a significant reaction (see, e.g., USP 4,183,876).

USP 4,130,534 describes TPVs compositions, called, however, "elastomeric compositions", comprising crystalline polyolefins and butyl or halobutyl rubber, made by DV, e.g., in extruder, or not. Curing agents are listed at col. 7, lines 20-42.

USP 4,130,534 describes TPVs of olefin rubber and polyolefin resins, with many examples and details.

USP 4,183,876, applied for in 1978, is more general than the two previous ones. It uses DV, though not necessarily, and mentions many possible alternatives, but the claims are limited to polyalkenamer rubber, defined as "random noncrystalline, rubbery polymer of cycloalkene". Dynamic vulcanization is described as "masticating" the blend of components, e.g. in extruders, "at a temperature sufficient to effect cross-linking formation".

USP 5,066,700 discloses a process comprising making a mixture of 1) PP or PET-PP; 2) ethylene-propylene elastomeric copolymer or -diene elastomeric terpolymer; 3) peroxide; 4) furan derivative; masticating while heating, and adding oil.

USP 4,803,244 discloses cross-linking the rubber component by hydrosilylation, viz. adding a silicon hydride across a multiple bond, often with a transition catalyst. An example is rhodium-catalyzed hydrosilylation of EPDM rubber in blend with PP.

USP 6,147,160 improves on USP 4,803,244 by a) suggesting specific copolymers of, e.g., isobutylene and divinylbenzene; b) hydrosilylating them with Pt catalyst.

USP 6,331,595 discloses grafting a monomer which may be a vinyl trialkoxy silane, onto a polyolefin, using as a catalyst an organic peroxide coated onto a carrier polymer.

While the literature on TPVs is very extensive, no fully satisfactory process is available in the art. DV is preferable to other systems, but there are difficulties in carrying out full vulcanization of the elastomers used. Prior art DV involves at least one of the following significant disadvantages. In

some cases phenolic resins are used in this reaction, and they are toxic. In other processes, tin dichloride is used and results in hygroscopicity of the TPVs. Some processes lead to discoloration or staining of the finished product and it is very difficult to obtain a product having a natural white color. In other processes, the elastomers have poor UV resistance. Finally, prior art processes do not permit the use of a wide range of matrices and cross-linkable components.

It is therefore the purpose of this invention to provide a process that is free from all the aforesaid disadvantages and that permits the use of a wide range of raw materials.

It is another purpose to provide a process that is easily carried out and uses standard equipment, such as extruders, and that can be implemented continuously.

It is a further purpose to provide a process which causes 100% cross-linking of the elastomer within a short residence time and which permits to use low contents of cross-linking catalysts.

It is a still further purpose to provide a final TPV product that has a combination of physical properties that will be set forth hereinafter.

Other purposes and advantages of the invention will appear as the description proceeds.

Summary of the Invention

The process of the invention comprises dynamic vulcanization (DV) of the disperse phase polymer (which may be elastomer) that will be a component or components of the final TPVs, in presence of the matrix polymer that will be another component of said TPV's, which DV comprises the steps of grafting an organic silane, particularly an alkoxy silane, on the disperse

phase polymer, whereby to form grafted polymeric chains, and then completing the vulcanization by cross-linking the grafted polymer chains. Both the grafting and cross-linking are carried out in the melt state at elevated temperature, either in batch or continuous mode, the latter being preferred. Preferably, in the batch mode the two reactions are performed successively in the same apparatus (for instance, a batch melt mixer), while in the continuous mode, the reactions are carried out preferably in an extruder (such as a twin screw, co-rotating, fully intermeshing extruder), but preferably are performed simultaneously in different zones of the extruder barrel. While reference will be made hereinafter to a disperse phase and a matrix material, this is done only for brevity's sake and should not be taken as a limitation, since more than one elastomer and more than one matrix material could be present in the TPVs of the invention. Also, the terms "matrix" and "disperse phase" should be understood as referring to the structure of the TPVs after phase inversion has occurred, since at the beginning of the process leading to the TPVs, and before the phase inversion, the phase structure of the blend may be quite different, so the component to be cross-linked may constitute a continuous phase in the initial blend, and the crystalline component may be dispersed therein. Hereinafter the terms "disperse phase material" and a "matrix material", will designate, unless otherwise specified, the components that will constitute the disperse phase and the matrix, respectively, no matter whether the phase inversion, and the cross-linking of the cross-linkable component, have already occurred or not, in spite of the fact that before the phase inversion the "disperse phase material" may constitute the matrix and the "matrix material" may constitute disperse phase.

The disperse phase material may be a non-elastomer, or polymers which may be considered as not really being elastomers,, such as medium or high density polyethylene. In many preferred cases, however, it is an elastomer.

Likewise, the matrix material may be partially crystalline or semi-crystalline.

Further, the meaning to be given in this application to the terms "vulcanization", "grafting" and "cross-linking" must be clearly defined, since the same terms may be used differently in other technical documents. "Grafting" is used herein in its normal meaning: the addition to a base molecule (which often is a polymeric, molecular chain) of separate, generally smaller moieties, either as lateral appendages to said molecule, or as insertion into said molecules, said moieties essentially maintaining their basic structure. In the present case, the original, non-vulcanized chains are the base molecules and the silane moieties are laterally attached to them or inserted into them by said grafting. "Cross-linking" is the following step: the silane-grafted, polymer chains are connected to one another through the silane moieties, by the action of a cross-linking agent, whereby to form a reticular structure. "Vulcanization" means herein the succession of grafting and cross-linking. The non-vulcanized polymers might also be called "polymer precursors", since they are the starting material from which vulcanized polymers are produced, but such a term will generally be avoided as it may be confusing.

The matrix materials (or briefly, "matrix") and the non-vulcanized, disperse phase components are chosen as follows. The matrix material is typically a partially crystalline or semi-crystalline polyolefin, examples of which will be given hereinafter. The matrix material may be from 20 to 80 wt% of the total polymeric mixture, viz. of the sum of the matrix material and the disperse phase component or components. Preferably, however, it is from 30 to 70 wt%. Higher matrix contents cause loss of advantages of the TPV, such as resilience and rubber-like behavior.

The disperse phase component can also be chosen from a large number of polymers, examples of which will be given hereinafter. Its content should

be from 20 to 80 wt% of the whole polymeric mixture, but is preferably from 30 to 70 wt%.

The grafting of silane onto disperse phase component is carried out by means of silanes, particularly alkoxy silanes, such as vinyl trimethoxy silane (VTMOS), vinyl triethoxy silane (VTEOS) and their blends, or methacryl silanes. The content of organic silane in the initial composition of raw materials is preferably 0.5 to 2.0 parts per 100 parts of total polymeric material.

The cross-linking of the grafted elastomer requires the presence of a cross-linking agent. The cross-linking agent of this invention is normally solid. According to the invention, said agent is a polyfunctional acid compound, optionally in combination with an amine compound. The acid compound is chosen from the group consisting of boric acid and combinations of organic, polyfunctional acids or their anhydrides. Examples of such organic acids are adipic, phthalic and pyromellitic acids. Boric acid is the most preferred. Examples of said amine compounds are triisopropanol amine or triethanol amine. The amount of cross-linking agent is preferably from 0.05 to 5, and more preferably from 0.1 to 0.5, parts per 100 parts of total polymeric content of the mixture.

Additional components may be added, as will be better explained hereinafter, and they may comprise antioxidants, plasticizers, mineral fillers and functional components.

In the process of the invention, the grafting and cross-linking of the disperse phase polymer are performed in the melt state at high temperatures, in batch or in continuous mode. If carried out in batch mode, the two stages of grafting and cross-linking are carried out successively; if carried out in continuous mode, the two stages are carried

out in different zones of the barrel of an extruder, or in similar conditions if a different apparatus is used.

In order to assure high selectivity of the grafting reaction, the matrix polymer should be chosen to be not cross-linkable or a disperse phase component should be chosen, the melting point of which is lower than that of the matrix polymer. In this latter case, the grafting temperature should be higher than the melting point of the disperse phase component but not higher, and preferably lower, than the melting point of the matrix component, viz. should be between the melting points of the two polymers, to assure that the matrix remains mainly solid and the possibility of silane grafting on it is strongly reduced.

The cross-linking stage starts when the cross-linking agent is added to the reaction mixture. At this stage the reaction temperature should be raised to a level at which all polymer components are melted.

Preferably, any remains of volatile components in the product should be removed by venting or vacuum, preferably after the grafting stage has ended. Extender oil may be added to the mixture after grafting stage and preferably after removal of the volatile components. Mineral fillers may be added, and antioxidants may be added after the grafting step.

The invention further comprises a final TPV having a set of physical properties that will be specified hereinafter.

Detailed Description of Preferred Embodiments

To provide rubber-like performance, the matrix and disperse phase polymers should preferably be thermodynamically incompatible and the final TPV product should preferably have the following properties:

low rigidity, high flexibility measured by low Shore hardness (usually TPVS have Shore hardness between 35A and 40D);

high disperse phase content (50% and more by volume);
high gel content of the vulcanized disperse phase component (the gel is the fraction insoluble in solvents, e.g., boiling xylene); if the gel content is more than 95%, the material is defined as "fully cross-linked"; otherwise, it is defined as "partially cross-linked";
high cross-link density of said vulcanized disperse phase component measured as knots concentration per cm^3 or molecular weight between knots (M_c);
cross-link density of the TPV of more than $5 \cdot 10^{-5} \text{ mol/cm}^3$, preferably more than $8.5 \cdot 10^{-5} \text{ mol/cm}^3$, more preferably more than $10 \cdot 10^{-5} \text{ mol/cm}^3$;
a disperse phase consisting, after phase inversion, of fine and uniform particle size (of few microns to submicron), preferably between 0.2 and 2 microns;
white color, lack of hygroscopicity and of toxic components;
and
there should be narrow gaps (ligaments) between cross-linked disperse phase particles, providing near-continuity of said particles within the matrix.

As matrix materials, the majority of semi-crystalline polymers are suitable. Examples are: thermoplastic polyesters, polyacetals, polyvinylidene fluoride (PVDF), crystalline polyethylene, ethylene copolymers, etc.; but polypropylene homopolymer, propylene-ethylene random copolymer (up to 4% ethylene), heterophasic propylene-ethylene (up to 25% of EPR), polyamides are preferred.

The content of matrix material should be 20 to 80wt%, but preferably 30 to 70wt% of the total polymeric composition (matrix plus cross-linkable components). If the matrix content is below said ranges, it is difficult to prevent the cross-linked phase from remaining continuous. If the matrix

content is above said ranges, the advantages of TPVS, such as resilience and rubber-like behavior, are lost.

The disperse phase polymer, to be vulcanized, is preferably chosen from: ultra-low density ethylene-alpha-olefin copolymers – including ultra-low density polyethylene (ULDPE), very low density polyethylene (VLDPE), medium density polyethylene (MDPE), and linear low density polyethylene (LLDPE) – EPDM, EPR, styrenic block-copolymers (SBS), low density polyethylene (LDPE), high density polyethylene (HDPE), ethylene-vinyl acetate copolymers (EVA) and their blends, chlorinated polyethylene (CPE), styrene-(ethylene-butylene), styrene block copolymer (SEBS), acrylic elastomers, ethylene-acrylate copolymers, nitrile rubber, styrene-butadiene rubber, chloroprene rubber, butyl rubber, polybutadiene, natural rubber.

In the initial polymeric mixture the content of the disperse phase component should be 20 to 80wt%, but preferably 30 to 70wt% of the total polymeric mixture (matrix plus cross-linkable elastomers).

As has been said, the process of the invention may be carried out in batch mode, as follows.

All the initial polymeric components (matrix and disperse phase component) are mixed with the chosen silane, free radicals generator and, optionally, tin-organic catalyst. The matrix may be fed in this stage only in part and the required amount be completed later. The ratio of the first to the second amount may vary e.g. from 1:10 to 10:1, but it is preferable that the amount fed in the first stage be at least 40wt% of the total. The mixing of all the aforesaid components may be carried out in any convenient device, e.g. in a batch melt mixer equipped by roller or another mixing elements and heated to a suitable temperature. Most suitable temperatures are those at which the disperse phase component is molten, but the matrix is not molten or at least not totally. This means,

temperatures between the melting point of the disperse phase component and that of the matrix. The grafting reaction begins with the mixing and lasts from a few minutes to half an hour. A free radical generator, e.g. an organic peroxide, should be present in the grafting stage, preferably in an amount of 0.05 to 0.2 parts per 100 parts of total polymers. After the end of the grafting, the temperature of the mixture is raised to at least the melting point of the matrix, and the cross-linking agent and an antioxidant of any class known in the art (e.g. hindered phenols, organic phosphites, thioethers or blends thereof) are added. An antioxidant is preferably, though not necessarily, added to the reagents after the grafting step. Its purpose is to protect the final product from thermo-oxidative degradation, and it will also help to neutralize any excess peroxide. If only a part of the matrix was initially fed, the required completion amount is fed at this stage. Cross-linking agent is added at this stage. The antioxidant neutralizes the peroxide, thus completing the grafting reaction, and the cross-linking agent together with the optional hydrolysis catalyst provide cross-linking of the elastomeric phase, while phase inversion occurs. The cross-linking step is accompanied by a significant rise in torque; then the torque stabilizes and may even slightly decrease, signaling that the reaction is finished. The duration of the cross-linking stage may vary from a few minutes to half an hour. Then the reaction mixture can be devolatilized by air venting. Subsequently, extenders, fillers and other additives, if required, are added and thoroughly mixed with the said reaction mixture. The final product is discharged from the mixer, processed in any desired way (e.g., on roll mill), cooled and pelletized.

The process of the invention can be carried out in continuous mode, as follows.

All the initial polymeric components (matrix and disperse phase component) are fed to the chosen heating and mixing device, preferably are fed gravimetrically into the main hopper of a twin-screw co-rotating fully

intermeshing extruder. While an extruder will be referred to hereinafter, this should not be considered a limitation, as other continuous heating-mixing devices could be used. The matrix may be fed in this stage only in part and the required amount be completed later, as hereinbefore set forth. Silane and peroxide, optional tin-organic catalyst may be fed in dry blend with polymers (pre-mixed) or pumped directly into the grafting zone of the extruder, or other equipment, via a metering pump. Gravimetric feeding, however, is preferred. The cross-linking agent is added after the grafting step has been completed. The feeding zone of the extruder is cooled (preventing bridging). The following zone of the extruder is the grafting zone, which is heated to a such a temperature as to melt the disperse phase without melting the matrix. The said grafting zone is equipped with parts, such as kneading segments, to thoroughly mix the blend. The temperature of the grafting zone may increase significantly due to reaction heat, and if so it may be cooled. After the grafting zone, an additional feeder zone is provided, into which are fed the additives needed for causing cross-linking, including cross-linking agents and antioxidants. Preferably, the said additives are dry blended with the amount of matrix required for completion, if any, and the blend is fed gravimetrically to said feeder zone by free gravitation flow or compulsory via side feeder. The latter is preferable, because it is hermetical and prevents volatile components removal via the feeding ports of said additional feeder zone (hereinafter, also, "second feeding ports") to distinguish then from the feeding ports of the feeder zone of the extruder (hereinafter, also, "first feeding ports"). In any case, screws in the feeding zone should have enough free volume to permit the said feed. The temperature in this zone, in the case of a side feeder, is preferably lower than the matrix melting point, to prevent a melt from plugging the feeding screws. The overall amount of matrix can be split between first and second feeding ports in any ratio between 1:10 and 10:1. Preferable 10-20wt% of the total matrix polymer is fed via said second feeding ports. After the said additional feeding zone the extruder comprises a mixing (cross-linking) zone equipped with kneading blocks and

heated to a significantly higher temperature, preferably a temperature that is higher by at least 10°C than the melting point of the matrix component. The following extruder zone is a devolatilization zone designated for volatiles removal. It should have enough free volume to prevent material entrance to the venting ports. Either atmosphere or vacuum vent can be applied. Extender oil can be pumped into the extruder, in a zone also having free volume for oil introduction, the oil injection zone being isolated from the venting zone to prevent oil venting. After the oil addition, the extruder should include a significant mixing zone. Then additional oil may be injected, if the barrel length allows this. Alternatively, the latter operations can be performed in another extruder or via a separate run. The filler, which may be any filler used in the present TPV art, e.g. calcium carbonate, talc or clay, can be added either via dry blend or via side feeder. The final product is continuously extruded through a die plate, cooled and pelletized either by strand or by the die-face pelletizing method. The overall time of the process may be from 1 to 5 minutes.

The following examples illustrate but do not limit the invention.

EXAMPLES

Example 1 (basic).

The first mixture of 60 parts by weight of ethylene-octene copolymer (Engage 8842 ex. DuPont Dow Elastomers), 25 parts by weight of random propylene-ethylene copolymer (MFI 0.3 at 230°C, 2.16 kg; 3.5% ethylene, ex. Carmel Olefins Ltd.), 1.0 parts by weight of vinyl trimethoxy silane (VTMO), 0.08 parts by weight of 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane (Luperox 101 ex. Atofina Chemicals) and 0.03 parts by weight of dibutyltin dilaurate (DBTDL), prepared by dry mixing, was fed to the main feeding port of fully intermeshing co-rotating twin-screw extruder (Berstorff ZE25*32). Feeding rate 6.0 kg/h, screws speed 350 rpm.

The second mixture containing 15 parts by weight of random propylene-ethylene copolymer, 0.4 parts by weight of boric acid, 0.4 parts by weight of Irganox B225 antioxidant (ex. Ciba Specialty Chemicals), 0.1 part by weight of calcium stearate and 0.1 part by weight of ethylene-bis-stearamide (EBS) was fed through the side feeder located at zone 4 of said extruder with the feeding rate 1.1 kg/h.

Volatile products were removed via vacuum port located at zone 6 of the extruder, equipped with vacuum pump.

Mineral oil (Primol 262) was fed under pressure via injection port located at zone 7 of the extruder by means of a metering pump with the rate providing an output of 168 g/min, i.e., 42 parts by weight of the oil per 100 parts of total polymers.

The resulting molten and homogenized mixture was extruded via three-hole die producing strands that were cooled in the cooling bath, dried online by vacuum drier and cut on the pelletizing machine producing pellets.

Barrel temperatures (zone 1 to zone 8, set points): 50-150-150-150-180-200-200-200°C. Die temperature: 200°C.

The resulting pellets were then injection molded to provide samples for mechanical and other tests. The pellets were also extruded through flat die into film (0.3 mm thickness, 30 cm width) on a single-screw extruder to check processability and film surface quality. The testing results of the obtained product are summarized in Table I.

Examples 2-5: Different ratios of polymer components.

The procedure is according to Example 1, but with different amounts of the same ethylene-octene copolymer and random propylene-ethylene copolymer in the first mixture. The compositions and testing results of the obtained product are summarized in Table I.

Table I:
Compositions and testing results for Examples 1-5 (parts by weight)

Component	Example 1	Example 2	Example 3	Example 4	Example 5
First Mixture					
Ethylene-octene copolymer	60	40	50	65	70
Random propylene-ethylene copolymer	25	45	35	25	15
VTMO	1.00	1.00	1.00	1.00	1.00
Luperox 101	0.08	0.08	0.08	0.08	0.08
DBTDL	0/03	0.03	0.03	0.03	0.03
Second Mixture					
Random propylene-ethylene copolymer	15	15	15	15	15
Boric acid	0.40	0.40	0.40	0.40	0.40
Irganox B225	0.40	0.40	0.40	0.40	0.40
EBS	0.10	0.10	0.10	0.10	0.10
Mineral oil	42	26	27	52	10
Properties					
Gel content in dispersed phase, %	99	100	98	98	94
Crosslink density, Mc	9884	9190	8648	11637	10253
Hardness Shore A	78	92	88	65	78
Hardness Shore D		32	26		27
Tensile strength, MPa	9.2	13.6	9.1	5.4	8.1
Elongation at break, %	246	493	320	249	187
Stress at 100%, Mpa	6.3	7.0	5.7	3.7	6.1
Tension set, %		64.1	58.2	63.0	62.8
Compression set, %	57	64	45	43	

Examples 6-8, Different polypropylene types.

The procedure is according to Example 1, but with different types of propylene polymers instead of random propylene-ethylene copolymer in the first and second mixtures. The compositions and testing results are summarized in Table II.

Table II:
Compositions and testing results for Examples 6-8

Components	Example 6	Example 7	Example 8
First mixture			
Random propylene-ethylene (MFR 0.3 dg/min, 3.5% ethylene) – PP-R	30		
Heterophasic propylene-ethylene copolymer (MFR 4 dg/min, 13% ethylene) – PP-B		30	
Polypropylene homopolymer (MFR 2 dg/min) – PP-H			30
Ethylene-octene copolymer (Engage 8842)	50	50	50
VTMO	1.00	1.00	
Luperox 101	0.08	0.08	0.08
DBTDL	0.03	0.03	0.03
Second mixture			
Random polypropylene-ethylene (MFR 9 dg/min, 3.5% ethylene)	15		15
Heterophasic propylene-ethylene copolymer (MFR 4 dg/min, 13% ethylene)		15	
Boric acid	0.30	0.30	0.30
Irganox B225	0.50	0.50	0.50
Calcium Stearate	0.10	0.10	0.10
Maleic anhydride grafted PP (Fusabond MZ203D)	5.00	5.00	5.00
Mineral oil	32.5	29	34
Properties			
Gel content in dispersed phase, %	100	100	100
Hardness Shore A	88	85	87
Hardness Shore D	28	26	28
Tensile strength, MPa	9.7	7.2	7.8
Elongation at break, %	326	227	263
Stress at 100%, Mpa	5.9	5.0	5.1
Tension set, %	56.7	52.5	67.1

Examples 9-11. Different types of cross-linked elastomers.

The procedure according to Example 1, but with different elastomers instead of ethylene-octene copolymer in the first mixture. The compositions and testing results are summarized in Table III.

Table III
Compositions and testing results for Examples 9-11.

Components	Example 9	Example 10	Example 11
First mixture			
Random propylene-ethylene copolymer	35	35	35
Styrene-butadiene-styrene block copolymer, 30% styrene (Europrene SOL T166 ex. Enichem)	50		
Styrene-butadiene-styrene block copolymer containing 45% of mineral oil (Europrene SOL T172 ex. Enichem)		72	
Ethylene-propylene-diene terpolymer (Nordel IP3720 ex. DuPont Dow Elastomers)			50
VTMO	1.00	1.00	1.00
Luperox 101	0.08	0.08	0.08
DBTDL	0.03	0.03	0.03
Second mixture			
Random polypropylene-ethylene copolymer	15	15	15
Boric acid	0.3	0.3	0.3
Irganox B225	0.5	0.5	0.5
Ethylene bis-stearamide (EBS)	0.1	0.1	0.1
Mineral oil	42.8	89	23
Properties			
Gel content in dispersed phase, %	86	55	74
Crosslink Density, Mc	2870	7290	28400
Hardness Shore A	90	86	90
Hardness Shore D	31	25	29
Tensile strength, MPa	13.0	9.1	9.1
Elongation at break, %	315	376	500
Stress at 100%, Mpa	8.1	5.8	6.0
Tension set, %	40.3	54.5	63.8
Compression set, %	52	50	68

Examples 12-21. Additional types of cross-linked polymers.

The procedure is according to Example 1, but with different polymers instead of ethylene-octene copolymer in the first mixture. The compositions and testing results are summarized in Table IV.

Table IV
Compositions and testing results for Examples 12-21.

Comp.	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21
First mixture										
P-R	35	35	35	35			25	15	35	35
P-B										
P-H						35				
E1	50				35					
E2		50					60	70		
E3			50		50	50				
E4				50						
E5									50	
E6										50
TMO	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
up. 101	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
BTDL	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Second mixture										
P-R	15	15	15	15	15	15	15	15	15	15
us. 203D	1	1	1	1	1	1	4	4		
oric acid	0.30	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
g. B225	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
a. Stear.	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10		
BS	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Properties										
el content dispersed phase, %	100	99	100	97	100	100	83	79	100	100
ardness shore D	58	57	57	56	57	56	57	54	59	64
ensile length, Pa	19.3	21.7	19.8	19.7	18.0	17.6	16.3	15.9	24.2	27.6
longation at break, %	427	445	401	423	436	365	304	229	250	145
length at eld line, Pa	14.4	14.6	17.4	15.2	15.9	14.2	13.2	12.0	19.8	21.6
longation at eld line, %	64	125	395	265	190	145	29	46	120	30

In this table: PE – Low density polyethylene (MFR 0.3 dg/min at 190°C, 2.16 kg) ex. Carmel Olefins Ltd.;

PE2 – Linear low density polyethylene (MFR 1.0 dg/min at 190°C, 2.16 kg) ex. Enichem;

PE4 – Metallocene linear low density polyethylene (Evolue, MFR 1.0 dg/min at 190°C, 2.16 kg) ex. Mitsui Petrochemical;

PE5 – Medium density polyethylene (MFR 1.0 dg/min at 190°C, 2.16 kg) ex. TVK;

PE6 – High density polyethylene (MFR 0.3 dg/min at 190°C, 2.16 kg) ex. LG Chemicals.

Examples 22-28. Different amounts of silane, peroxide, catalyst.

The procedure is according to Example 1, but with different amounts of VTMO, Luperox 101 and DBTDL in the first mixture. Also different types of silane and peroxide were used. The compositions are summarized in Table V.

Table V
Compositions and testing results for Examples 22-28

Components	Ex. 22	Ex. 23	Ex. 24	Ex. 25	Ex. 26	Ex. 27	Ex. 28
First Mixture							
PP-R	25	25	25	25	30	35	35
Engage 8842	60	60	60	60	55	50	50
VTMO	1.0	1.25	1.50	1.25		1.20	1.20
Vinyl trethoxy silane (VTEO)					1.20		
Luperox 101	0.10	0.10	0.10			0.10	0.10
Dicumyl peroxide				0.10			
Perkadox 14S ex. Akzo					0.10		
DBTBL	0.025	0.025	0.025	0.025	0.08		0.08
Second Mixture							
PP-R	15	15	15	15	15	15	15
Boric acid	0.40	0.40	0.40	0.40	0.3	0.3	0.3
Irganox B225	0.50	0.50	0.50	0.50	0.40	0.50	0.50
EBS	0.10	0.10	0.10	0.10	0.1	0.1	0.1
Fusabond MZ203D					3.0		
Mineral oil	35	35	35	40	13	40	40
Properties							
Gel content in dispersed phase %	100	100	100	93	62	100	100
Crosslink density, Mc	10022	11292	8115	9480	21485	8912	8620
Hardness Shore A	70	70	70	78	93	83	85
Hardness Shore D					34	24	25
Tensile strength, MPa	6.1	6.4	6.5	7.8	10.1	5.7	6.3
Elongation at break, %	251	265	244	254	408	294	243

Stress at 100% MPa	3.9	4.3	4.2	5.6	7.4	3.7	4.1
Tension set, %	63	62	52	46	46	55.2	57.5
Compression set, %	49	41	38				

Examples 29-33. Additional components.

The product obtained by the procedure described in Example 1 was extruded a second time on the same extruder with the addition of fillers and an additional amount of mineral oil. The compositions and testing results are summarized in Table VI.

Table VI
Compositions and testing results for Examples 29-33

Components	Ex. 29	Ex. 30	Ex. 31	Ex. 32	Ex. 33
First Mixture					
PP-R	20	20	20	25	25
Engage 8842	65	65	65	60	60
VTMO	1.3	1.3	1.3	1.0	1.0
Luperox 101	0.11	0.11	0.11	0.08	0.08
DBTBL	0.04	0.04	0.04	0.03	0.03
Second Mixture					
PP-R	15	15	15	15	15
Boric acid	0.40	0.40	0.40	0.40	0.40
Irganox B225	0.50	0.50	0.50	0.50	0.50
EBS	0.10	0.10	0.10	0.10	0.10
Mineral oil	50	50	50	26	26
Second pass.					
Calcium carbonate	15			19	19
Kaolin		15			
Talc			15		
Mineral oil					
Properties					
Gel content in dispersed phase %	100	100	100	95	95
Crosslink density, Mc	8649	9485	8913	10232	9659
Hardness Shore A	75	76	79	85	77
Hardness Shore D				24	22
Tensile strength, MPa	6.4	6.8	7.0	8.1	6.2
Elongation at break, %	190	200	190	279	271
Stress at 100% MPa	4.7	4.9	5.5	5.3	3.9
Tension set, %	54.8	53.2	52.5	68.1	71.8
Compression set, %				49	56

Examples 34-40. Different cross-linking agents.

The procedure is according to Example 1, but with different cross-linkers instead of boric acid.

The compositions and testing results are summarized in Table VII.

Table VII
Compositions and testing results for Examples 34-39

Components	Ex. 34	Ex. 36	Ex. 37	Ex. 38	Ex. 39	Ex. 40
First Mixture						
PP-R	35	35	35	35	35	20
Engage 8842	50	50	50	50	50	60
VTMO	1.2	1.2	1.2	1.2	1.2	1.2
Luperox 101	0.10	0.10	0.10	0.10	0.10	0.10
DBTBL	0.08	0.08	0.08	0.08	0.08	0.08
Second Mixture						
PP-R	15	15	15	15	15	20
Irganox B225	0.50	0.50	0.50	0.50	0.50	0.50
Ca. Stearate.	0.10	0.10	0.10	0.10	0.10	0.10
Primacor* 3460	3.00					
SMA 2000**						
Phthalic anhydride		0.20				
Adipic acid			0.20			
Melamine				0.20		
Pyromellitic acid					0.20	
TIPA***						0.40
Properties						
Gel content in dispersed phase %	71	78	80	77	85	83
Crosslink density, Mc	8041	10869	9489	11886	12303	15719
Hardness Shore A						
Hardness Shore D	46	46	46	46	46	46
Tensile strength, MPa	12.0	14.9	13.9	15.8	13.7	12.5
Elongation at break, %	>500	>500	>500	>500	>500	399
Stress at 100% MPa	8.4	8.9	8.4	8.7	8.7	7.5
Tension set, %	71	67	71	69	71	50

*Primacor 3460 is ethylene-acrylic acid copolymer ex. Dow Chemicals

**SMA 2000 is styrene-maleic acid anhydride copolymer ex. Atofina

***TIPA is triisopropanol amine

Example 41. Two-step process.

The mixture of 50 parts by weight of ethylene-octene copolymer (Engage 8842 ex. DuPont Dow Elastomers), 50 parts by weight of random propylene-ethylene copolymer (MFI 0.3 at 230°C, 2.16 kg; 3.5% ethylene, ex. Carmel Olefins Ltd.), 1.2 parts by weight of vinyl trimethoxy silane (VTMO), 0.1 part by weight of 2,5-dimethyl-2,5-di-(tertbutylperoxy)hexane (Luperox 101 ex. Atofina Chemicals) and 0.08 parts by weight of dibutyltin dilaurate (DBTDL), prepared by dry mixing, was fed to the main feeding port of fully intermeshing co-rotating twin-screw extruder (Berstorff ZE25*32). Feeding rate – 5.0 kg/h, screws speed – 350 rpm.

Mineral oil (Primol 262) was fed under pressure via injection port located at zone 7 of the extruder by means of a metering pump with the rate providing output of 102 g/min, i.e., 23 parts by weight of the oil per 100 parts of total polymers.

The resulting molten and homogenized mixture was extruded via three-hole die producing strands that were cooled in the cooling bath, dried online by vacuum drier and cut on the palletizing machine producing pellets.

Barrel temperatures (zone 1 to zone 8, set points): 50-130-140-150-180-200-200-200°C. Die temperature – 200°C.

101.38 parts by weight of the obtained pellets were mixed with 0.3 parts of boric acid, 0.50 parts of Irganox B225, 0.1 part of calcium stearate and 0.1 part of Primol 262 mineral oil and extruded on the same extruder at temperatures 50-180-190-190-190-190-190-190°C and die temperature 190°C with screws speed 300 rpm and throughout 10 kg/h to obtain the final palletized product.

190°C with screws speed 300 rpm and throughout 10 kg/h to obtain the final palletized product.

The testing results of the obtained product are summarized in Table VIII.

Examples 42-49. Variations of two-step process.

The procedure is according to Example 41 with various components, with additional oil and/or mineral filler on the second extrusion step. The compositions and testing results are summarized in Table VIII.

Table VIII
Compositions and testing results for Examples 43-49

Components	Ex. 41	Ex. 42	Ex. 43	Ex. 44	Ex. 45	Ex. 46	Ex. 47	Ex. 48	Ex. 49
First step									
P-R	50	50	50	50	50				50
P-B						50	50		
P-H								50	
Agage 8842	50	50	50	50	50	50	50	50	50
TMO	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
perox 101	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
BTBL	0.03	0.03	0.03	0.03	0.03	0.03	0.08	0.03	0.08
Mineral oil	23								39
Second step									
Step product	123	101.38	101.38	101.38	101.38	101.38	101.38	101.38	101.38
oric acid	0.30	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
ganox B225	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
alcium stearate	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
alcium carbonate			20		20				
Mineral oil				25	25		19		
Properties									
el content in dispersed phase %	87	100	100	100	94	100	100	100	91
rosslink density, c	14271	11697	8550	13261	12934	11782	11036	4783	14418
ardness Shore A	90			89	89		90	94	90
ardness Shore D	31	46	46	30	30	46	36	39	33
nsile strength, Pa	7.4	15.8	15.6	9.5	8.7	13.1	9.8	12.7	7.9
ongation at break, %	364	367	322	338	295	248	208	165	350
ress at 100% Pa	4.9	9.9	10.5	5.8	5.5	9.2	7.1	10.1	5.1
nsion set, %	53	62	67	52	46	61	52	54	53

Example 50. Batch process.

0.05 g Luperox 101 and 0.03 g DBTDL were introduced into the batch mixture (Haake Rheomix 600) equipped with two roller blades at 180°C and 20 rpm. Then the speed of the blades was increased to 100 rpm for the time period of 10 minutes. After this, 0.2 g of adipic acid and 0.2 g of Irganox B225 were added to the mixture and the blend was mixed for another 10 minutes at 150 rpm. After that the molten blend was discharged from the mixer and compression molded into the plate (thickness 2 mm). The samples for testing were cut from this plate. The testing results of obtained product are summarized in Table IX.

Examples 54-66. Variations of the batch process.

The procedure according to Example 50 was performed with different cross-linking agents. The compositions and testing results are summarized in Table IX.

Table IX
Compositions and testing results for Examples 50-56.

Components	Ex. 50	Ex. 51	Ex. 52	Ex. 53	Ex. 54	Ex. 55	Ex. 56
First Period							
PP-R	40	40	40	40	40		
PP-B						40	
PP-H							40
Engage 8842	60	60	60	60	60	60	60
VTMO	1.20	1.60	1.60	1.60	1.00	0.95	0.95
Dicumyl peroxide	0.11	0.27	0.27	0.27	0.10	0.08	0.08
DBTBL	0.07	0.10	0.10	0.10	0.07	0.07	0.07
Second Period							
Irganox B225	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Calcium stearate	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Adipic acid	0.4		9.4	0.2	0.4	0.4	0.4
Triethanol amine		0.4		0.2	0.4	0.4	0.4
Properties							
Gel content in dispersed phase %	97	58	59	62	100	100	97
Crosslink density, Mc	8177	10832	8281	6602	4438	8308	8177

Control examples 57-58 (batch process).

The procedure is according to Example 50, but without cross-linking agent and/or without silane, peroxide and catalyst. The compositions and testing results are summarized in Table X.

Table X

Compositions and testing results for Examples 57-58

Components	Example 57	Example 58
First period		
Random propylene-ethylene copolymer	40	40
Ethylene-octene copolymer (Engage 8842)	60	60
VTMO		1.60
Dicumyl peroxide		0.27
DBTDL		0.10
Second period		
Irganox B225	0.40	0.40
Calcium Stearate	0.10	0.10
Properties		
Gel content in dispersed phase, %	0	30
Crosslink density, Mc		21348

In general, the vulcanizates of the invention have excellent properties, which include the following:

- a) low rigidity;
- b) high flexibility measured by low Shore hardness between 35A and 40D;
- c) disperse phase content of at least 50% by volume;
- d) high gel content of the vulcanized disperse phase component;
- e) high cross-link density measured as knots concentration per cm³ or molecular weight between of the vulcanized disperse phase component;
- f) white color;
- g) non-hygroscopicity;
- h) lack of toxic components;

- i) excellent processability by techniques used for processing thermoplastics, comprising extrusion, molding, thermoforming, blow molding, calendering;
- k) very good impact resistance at room temperature and below 0°C; and
- l) high melt elasticity and melt strength.

Particular embodiments have been described only to illustrate the invention and it is to be understood that the invention can be carried out with many modifications, adaptations and variations, without departing from its spirit or exceeding the scope of the claims.

CLAIMS

1. Process for the production of thermoplastic vulcanizates, which comprises preparing a mixture of polymeric materials, including a matrix and a disperse phase component, and carrying out dynamic vulcanization of the disperse phase component, said dynamic vulcanization comprising the steps of grafting an organic silane on said disperse phase component, whereby to produce grafted disperse phase component chains, and cross-linking said disperse phase component chains in the presence of a cross-linking agent, said grafting and said cross-linking being carried out in the molten state of said disperse phase component.
2. Process according to claim 1, wherein the organic silane is an alkoxy silane.
3. Process according to claim 1, wherein the cross-linking agent is a polyfunctional acid compound, optionally in combination with an amine compound.
4. Process according to claim 3, wherein the cross-linking agent is chosen in the group consisting of boric acid and of combinations of adipic acid and an amine.
5. Process according to claim 3, wherein the amine of the combinations of adipic acid and an amine are triisopropanol amine or triethanol amine.
6. Process according to claim 1, wherein the dynamic vulcanization is carried out in batch mode.
7. Process according to claim 1, wherein the dynamic vulcanization is carried out in continuous mode.

8. Process according to claim 1, wherein the matrix material is a semi-crystalline polymer.
9. Process according to claim 7, wherein the semi-crystalline polymer is chosen in the group consisting of thermoplastic polyesters, polyacetals, polyvynilidene fluoride (PVDF), crystalline polyethylene, ethylene copolymers, polypropylene homopolymer, propylene-ethylene random copolymer, heterophasic propylene-ethylene copolymer, and polyamides.
10. Process according to claim 7, wherein the semi-crystalline polymer is in the amount of 20 to 80wt% of the total polymeric composition.
11. Process according to claim 1, wherein the disperse phase component is chosen in the group consisting of ethylene-alpha-olefin copolymer, wherein said alpha-olefin contains 3 to 20 carbon atoms (ULDPE, VLDPE, LLDPE, MDPE), EPDM, EPR, styrenic block-copolymers (SBS), low density polyethylene (LDPE), , high density polyethylene (HDPE), ethylene-vinyl acetate copolymers (EVA) and their blends, chlorinated polyethylene (CPE), styrene-(ethylene-buthylene), styrene block copolymer (SEBS), acrylic elastomers, ethylene-acrylate copolymers, nitrile rubber, styrene-butadiene rubber, chloroprene rubber, butyl rubber, polybutadiene, natural rubber.
12. Process according to claim 7, wherein the crystalline polyolefin is in the amount of 20 to 80wt% of the total polymeric composition.

13. Process according to claim 1, wherein the disperse phase component is in the amount of 20 to 80wt% of the total polymeric composition.
14. Process according to claim 1, wherein the cross-linking agent is in the amount of 0.05 to 5 parts per 100 parts of the total polymeric composition.
15. Process according to claim 1, further comprising adding to the thermoplastic vulcanizate, at any convenient stage of the preparation thereof, one or more additional components chosen from the group consisting of antioxidants, plasticizers, mineral fillers and functional components.
16. Process according to claim 1, wherein the matrix is not cross-linkable.
17. Process according to claim 1, wherein the disperse phase component has a melting point lower than the melting point of the matrix and the grafting is carried out at temperatures between the melting point of the matrix and the melting point of the disperse phase component.
18. Process according to claim 1, wherein the grafting is carried out at temperatures at which all the polymeric components are molten.
19. Process according to claim 1, further comprising removing any remains of the volatile components by venting or vacuum after the grafting stage has ended.
20. Process according to claim 5; wherein the grafting and the cross-linking are carried out successively.

21. Process according to claim 6, wherein the grafting and the cross-linking are carried out in different zones of the barrel of an extruder.

22. Process according to claim 5, comprising the steps of:

- a) mixing the disperse phase component and at least part of the matrix with the chosen silane, free radicals, free radical generators and optionally tin-organic compounds;
- b) bringing the mixture of the aforesaid components to the grafting temperature;
- c) allowing the grafting to take place;
- d) after the grafting, raising the temperature of the mixture to at least the melting point of the matrix, and the cross-linking agent and antioxidant;
- e) allowing the cross-linking to occur, whereby phase inversion occurs;
- f) optionally, devolatilizing the resulting product;
- g) adding any required additional components, while mixing; and
- h) discharging the final product.

23. Process according to claim 6, comprising the steps of:

- a) feeding at least part of the matrix and all other polymeric components to the feed hopper of an extruder;
- b) feeding silane and peroxide to a feeding zone of the extruder, while cooling said zone;
- c) heating the grafting zone of the extruder such a temperature as to melt the disperse phase component without melting the matrix;
- d) kneading the resulting mixture;
- e) feeding an additional feeder zone of the extruder the additives needed for causing cross-linking, including cross-linking agents and antioxidants, while keeping said additional feeder zone to a the temperature lower than the matrix melting point;
- f) if necessary, completing the feeding of the matrix;

- g) mixing and kneading the mixture of the fed components, while heating;
- h) removing the volatiles removal;
- k) optionally, adding extender oil and mixing; and
- i) extruding the resulting product.

24. Thermoplastic vulcanizates, comprising two components, a matrix and a cross-linked disperse phase, which are thermodynamically incompatible, said vulcanizates having the following properties:

- a) low rigidity;
 - b) high flexibility measured by low Shore hardness between 35A and 40D;
 - c) disperse phase content of at least 50% by volume;
 - d) high gel content of the vulcanized disperse phase component;
 - e) high cross-link density measured as knots concentration per cm^3 or molecular weight between of the vulcanized disperse phase component;
 - f) white color;
 - g) non-hygroscopicity;
 - h) lack of toxic components;
- and

there are narrow gaps (ligaments) between cross-linked disperse phase particles, providing near-continuity of said particles within the matrix.

25. Thermoplastic vulcanizates, comprising two components, a matrix and a cross-linked disperse phase, which are thermodynamically incompatible, said vulcanizates having the following properties:

- a) low rigidity;
- b) high flexibility measured by low Shore hardness between 35A and 40D;
- c) disperse phase content of at least 50% by volume;
- d) high gel content of the vulcanized disperse phase component;
- e) high cross-link density measured as knots concentration per cm^3 or molecular weight between of the vulcanized disperse phase component;
- f) white color;
- g) non-hygroscopicity;

- h) lack of toxic components;
- i) excellent processability by techniques used for processing thermoplastics, comprising extrusion, molding, thermoforming, blow molding, calendaring;
- k) very good impact resistance at room temperature and below 0°C; and
- l) high melt elasticity and melt strength.

26. Thermoplastic vulcanizates according to claim 23, wherein the matrix consists of semi-crystalline polymers

27. Thermoplastic vulcanizates according to claim 23, wherein the semi-crystalline polymers are chosen in the group consisting of thermoplastic polyesters, polyacetals, polyvinylidene fluoride (PVDF), crystalline polyethylene, ethylene copolymers, polypropylene homopolymer, propylene-ethylene random copolymer, heterophasic propylene-ethylene copolymer and polyamides.

28. Thermoplastic vulcanizates according to claim 23, wherein the content of matrix is 30 to 70wt% of the total vulcanizate,

29. Thermoplastic vulcanizates according to claim 23, wherein the cross-linked disperse phase is chosen from the group consisting of ultra-low density ethylene-alpha-olefin copolymers (ULDPE), very low density polyethylene (VLDPE), EPDM, EPR, styrenic block-copolymers (SBS), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), ethylene-vinyl acetate copolymers (EVA) and their blends, chlorinated polyethylene (CPE), styrene-(ethylene-butylene), styrene block copolymer (SEBS), acrylic elastomers, ethylene-acrylate copolymers, nitrile rubber, styrene-butadiene rubber, chloroprene rubber, butyl rubber, polybutadiene, natural rubber.

30. Thermoplastic vulcanizates according to claim 23, wherein the content of the disperse phase is 30 to 70wt% of the total vulcanizate.

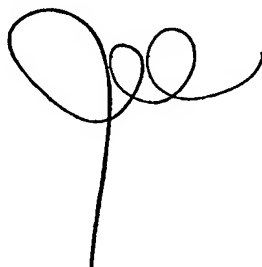
31. Products made from the thermoplastic vulcanizates of one or more of claims 1-30, by known processing techniques, including extrusion, injection molding, thermiforming, blow molding and calendaring.

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